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Nanostructured ZnO Photoelectrode Synthesis for Dye Sensitized Solar Cells

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The main aims of this work were to produce and examine the characteristics of nanostructured ZnO in dye-sensitized solar cells. Parameters which are affected by the efficiency such as precursor materials, morphology were investigated. The Raman spectroscopy was used to investigate transformation from bulk material to solution. General morphologies and detailed structural characterizations were obtained using field emission scanning electron microscopy. X-ray diffractometer has been used to determine preferred crystal orientation and particle size of the ZnO nanostructures.

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1. Introduction

ZnO is an important material and has received considerable attention due to its applications in electrical, optical, mechanical, and scientific research, as well as industry. ZnO is a wide band gap (3.37 eV) semiconductor and has a large binding energy (60 meV) [1], low resistivity and high transparency in the visible range and high light trapping characteristics [2]. ZnO has also attracted attention for electrical and optical applications such as light-emitting diodes, photocatalysts, photodetectors, piezoelectronic devices, sensors and solar cells [3].

Conventional solar cells are based on light harvesting and charge separation at semiconductor p–n junctions. In contrast, dye-sensitized solar cells (DSSCs) utilize a combination of wide-gap semiconductors and organic or metal-organic complex dyes which play a fundamental role in light harvesting [4].

DSSCs are unique compared with almost all other kinds of solar cells, in that electron transport, light absorption and hole transport are each handled by different materials in the cell. The sensitizing dye in a DSSC is anchored to a wide-bandgap semiconductor such as TiO_2, SnO_2, or ZnO [5]. TiO_2 still gives the highest efficiencies, but many other metal oxide systems have been tested, such as ZnO, SnO_2, and Nb_2O_5 [6]. Many researchers have tried to enhance the performance of ZnO-based DSSCs by modifying nanostructures of electrodes. For example, Kao et al. reported that the higher efficiency (η) of 2.5% was obtained by the ZnO film pre-annealed at 300 °C [7].

Nanostructured ZnO has been synthesized via a wide range of techniques [8]. Among these methods, the sol–gel method has drawn a considerable amount of attention in scientific and technological fields because of its considerable advantages of generally low temperature processing conditions, easy composition control and homogeneity, easy fabrication of thin films with large area and low cost [7].

In this paper, we aimed to produce and examine the characteristics of nanostructured ZnO in dye-sensitized solar cells.

2. Experimental details

2.1. Sol–gel derived nanocrystalline ZnO thin films

ZnO thin film coatings were synthesized by the preparation of ZnO sols in the liquid phase from homogeneous solutions with precursor of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$). Figure 1 represents the process flow chart used for synthesis of ZnO thin film coatings. Ethanol (C_2H_5OH) was used as solvent. The coating solution prepared by dissolving zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) in ethanol ($C_2H_5OH$) with 0.3, 0.5, and 0.7 M ratios. Certain amount of monoethanolamine (MEA) which acts as a base and a complexing agent [8] was added to solutions to change acid-base media and stirred for 1 h to form a clear, stable, and homogeneous sol at 60 °C. Sagar et al. [9] examined the role of pH value on the structural properties of ZnO films and investigated the basic nature of the modified sol as a function of increase in the ratio of additive MEA to ZnAc precursor. The increase in pH with addition of MEA indicated an increase of alkaline nature of the prepared sols. This increase was attributed to hydrolysis of salts of weak acid in strong base medium. The higher alkaline nature of sols was reported to be useful in enhancing the formation of ZnO crystallites [9]. In our study, MEA was added to sol until homogeneous and transparent solution was obtained.

Thin film deposition was carried out by dip coating route on fluorine-doped tinoxide-coated glass substrates (FTO substrates; Solaronix; sheet resistance of 7 $\Omega\,\mathrm{sq}^{-1}$) several times. Produced thin films were heat treated in a furnace at 400 °C. X-ray diffractometer (Rigaku

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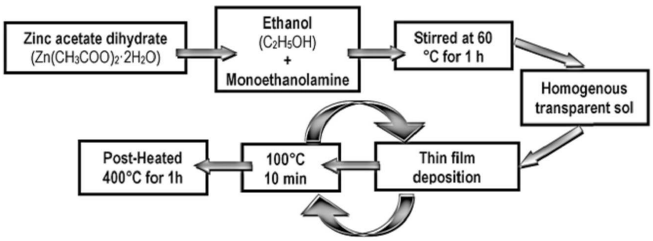

Fig. 1. The process flow chart used for synthesis of ZnO thin film coatings.

D/MAX 2000) was used to determine preferred crystal orientation and particle size of the thin films. The Raman spectroscopy was used to investigate transformation from bulk material to solution. General morphologies and detailed structural characterizations were obtained by using field emission scanning electron microscopy (FESEM). X-ray diffractometer was used to determine preferred crystal orientation and particle size of the thin films.

2.2. Preparing DSSC using ZnO photoelectrodes

For DSSC applications, ZnO thin films were sensitized by immersion in *cis*-diisothiocyanato-bis(2,2′-bipyridyl--4,4′-dicarboxylato)ruthenium(II) (also known as N719 in the literature; purchased from Solaronix) for a 12 h. For use as working electrode, the sensitized thin films were constructed to a cell device by assembling it with a counter electrode consisting of a thin carbon layer (Elcocarb C/SP; Solaronix) deposited on FTO glass. Sandwich cells were then prepared by sealing together the ZnO thin film coated electrode with the counter electrode using a transparent film of hot melt sealing foil (Meltonix; Solaronix) at 120 °C. The electrolyte solution (iodolyte Z-100; Solaronix) was then introduced through holes drilled in the counter electrode, which were sealed immediately with microscope cover slides. The final cells are referred to as "ZnO-1" as its photoelectrode was produced from 0.3 M solution, "ZnO-2" for photoelectrode produced from 0.5 M solution, and "ZnO-3" for photoelectrode produced from 0.7 M solution. Cells current–voltage characteristics were determined by illuminating with a AM 1.5-type simulated sunlight with 150 W xenon lamp (Oriel Newport Solar Simulator), equipped with an IR filter. Beam intensity was calibrated using an externally calibrated silicon photodiode. Current and voltage were measured and controlled using a Keithley 2400 source meter.

3. Results

Figure 2 presents the X-ray diffraction patterns of synthesized ZnO thin film coatings. The peak positions in each product agree well with the reflections of ZnO with all peaks corresponding well to standard crystallographic data (ZnO: JCPDS 00-036-1451). As could be seen from the X-ray diffraction (XRD) patterns, all products have polycrystalline nature, randomly oriented and peaks belonging to the (100), (002), (101), (102), (110) reflections are seen in ZnO. The random orientation is probably due to the difference in the precursor chemistry and heat treatment temperature [10]. (♦) symbol represents the diffraction peaks coming from FTO coated glass substrate. Furthermore, no other peak related to impurities is detected in the spectrum, which further confirms that the synthesized products are of high purity. There are changes in orientation and peaks intensities with the used different molar ratio of Zn-based solution. The peak intensities of the ZnO preferred orientation corresponding to the (100) and (101) planes were observed for all films. Znaidi [8] reported that all the production parameters play a role on the film orientation.

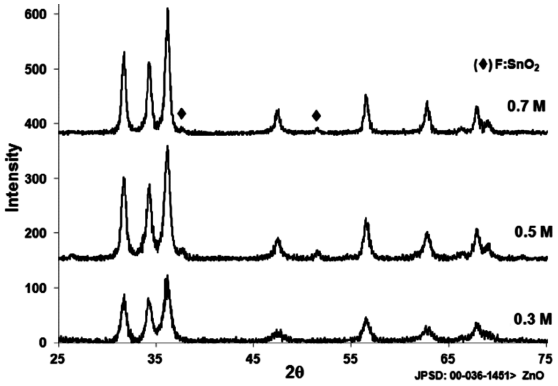

Fig. 2. The XRD diffraction patterns of thin film ZnO.

The Raman spectroscopy of zinc acetate dihydrate (coded as ZnAc) and Zn-based solutions (coded as 0.7 M ZnAc solution) were carried out to investigate transformation of the chemical compounds from the initiate material to the solution. Figure 3 represents the Raman spectrum of bulk ZnAc and Zn-based solution with 0.7 molar ratio.

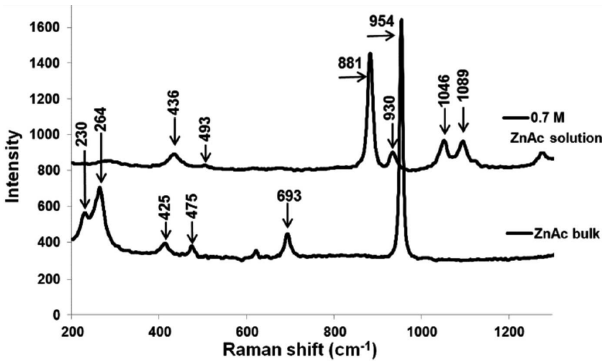

Fig. 3. Raman spectrum of ZnAc bulk and 0.7 M ZnAc solution.

The peaks at 881, 1046, and 1089 cm^{-1} correspond to the ethanol. The mode at 436 cm^{-1} in the dihydrate

has been assigned to the Zn–O bond, which is compatible with the literature [11]. When the zinc acetate dihydrate is dissolved in the ethanol, the E_2 mode shifts from 425 cm^{-1} to 436 cm^{-1} in the zinc acetate solution; this is due to the relaxation of the intermolecular stress. These bonds probably would initiate crystallization process during the films heat treatment [11].

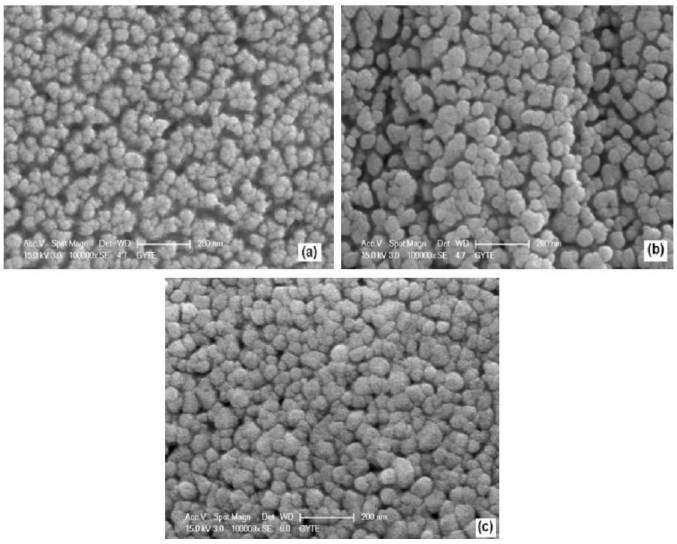

Fig. 4. FESEM images of ZnO thin films produced by using different molar ratio solutions: (a) ZnO-1, (b) ZnO-2, (c) ZnO-3.

As can be seen from Fig. 4a–c, the produced ZnO thin film coatings exhibit porous spherical nanostructures with the grain size 22 nm for ZnO-1, 28 nm for ZnO-2, and 31 nm for ZnO-3, which were calculated with Scherrer's formula. The rate of particle growth is governed by the concentration of precursors or dissolved species and their reactivity, which depends on the number of particle surface atoms, and the solution composition [8].

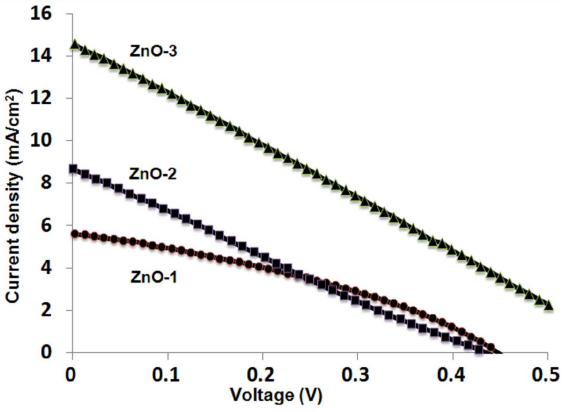

Fig. 5. J–V curves of the cells using ZnO electrodes produced from solution with different molar ratio.

The photovoltaic performance of cells using the ZnO electrodes was evaluated from the J–V measurements. J–V curves of the ZnO electrodes are shown in Fig. 5. The lowest cell performance was obtained from ZnO-3, V_{OC} is recorded as 0.44 V, J_{SC} is 5.841 mA/cm^2 and conversion efficiency is 0.63%. In the cell using the ZnO-2 electrode, V_{OC} recorded as 0.456 V while J_{SC} increases to 8.71 mA/cm^2 and the efficiency is 1.015%. The cell using ZnO-1 electrode shows V_{OC} of 0.59 V, J_{SC} of 14.58 mA/cm^2 and conversion efficiency of 2.2%.

4. Conclusions

Dye-sensitized solar cells were fabricated by using ZnO nanostructured thin film photoelectrodes synthesized from different molar ratio Zn-based sols. It is understood that the microstructures and also cell performances were dependent on the molar ratio of starting solution. The cell produced from zinc acetate dihydrate precursor, dissolved in ethanol with 0.7 M shows the highest conversion efficiency of 2.2%.

Acknowledgments

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